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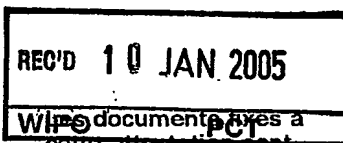
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A method, an immersion fluid and an apparatus for producing micro-chips

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A METHOD, AN IMMERSION FLUID AND AN APPARATUS FOR PRODUCING  
MICROCHIPS

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The invention relates to a method, an immersion fluid and an apparatus for producing microchips by using immersion lithography.

Since the invention of integrated circuits in 1959, the computing  
10 power of microprocessors has been doubled every 18 months and every three  
years a new generation of microchips has been introduced, every time reducing  
the size of electronic devices. This phenomenon is known as Moore's law. The  
performance of the microchip is, to a large degree, governed by the size of the  
individual circuit elements in the microchip. A microchip in general comprises as  
15 the circuit elements a complex three-dimensional structure of alternating,  
patterned layers of conductors, dielectrics, and semiconductor films. As a general  
rule, the smaller the circuit elements, the faster the microchip and the more  
operations it can perform per unit of time. This phenomenal rate of increase in the  
integration density of the microchips has been sustained in large by advances in  
20 optical lithography, which has been the method of choice for producing the  
microchips.

A higher degree of integration of the circuit requires a shorter  
wavelength of exposure light used in the method of producing microchips by  
optical lithography. Changing the exposure light to shorter wavelengths has  
25 indeed been the method of choice to increase the resolution. However, switching  
to shorter wavelengths is becoming increasingly a daunting task as new exposure  
tools and materials such as photo-resists must be designed. This is a difficult task  
and it often results in implementation issues and delays. Therefore chip  
manufacturers generally tend to postpone the introduction of a new exposure  
30 wavelength as long as possible and attempt to prolong the lifetime of an existing  
technology using alternative approaches. Already for a period of time immersion  
lithography is considered to be an effective method to improve the resolution limit  
of a given exposure wavelength. Here the air between the bottom lens and the  
silicon wafer having a layer of photoresist on top, in an apparatus is replaced with  
35 a fluid, leading essentially to a decrease in effective wave length, see for

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example: A. Takanashi et al. US Patent No. 4480910 (1984). The fluid should i.a. have a high transparency at least at the wavelength of the exposure light, it must not influence the chemistry of the photoresist on top of the silicon wafer, used to produce the microchip, it must not degrade the surface of the lens.

5                   Immersion lithography is for example possible for the wavelengths 248 nm, 193 nm and 157 nm. Because of its transparency at 193 nm water is the main candidate for immersion fluid at this wavelength. (See for example: J.H. Burnett, S. Kaplan, Proceedings of SPIE, Vol. 5040, P. 1742 (2003). Because of exceptional transparency of fluorinated and siloxane-based  
10 compounds at 157 nm, such fluids are being considered for 157 nm immersion lithography.

Aim of the invention is to provide a method for producing microchips by using immersion lithography showing further resolution enhancement.

15                   Surprisingly this aim is achieved because the immersion fluid comprises an additive so that the refractive index of the immersion fluid is higher than the refractive index of the fluid not comprising the additive.

Preferably the refractive index of the immersion fluid is at least 1% higher, more preferably at least 2% higher, still more preferably at least 5%  
20 higher, most preferably at least 10% higher than the fluid not comprising the additive.

Two types of additives may be added. Additives, which are soluble in the pure fluid, and additives, which are insoluble in the pure fluid and therefore must be dispersed as particles, preferably nano particles. As soluble  
25 additives, both organic compounds and liquids, and inorganic (salts) may be used. In case of water as fluid, examples of organic compounds include: various types of sugars, alcohols such as for example cinnamyl alcohol and ethylene glycol, 2-picoline, phosphorus or sulphur containing compounds, such as for example salts of polyphosphoric acids, sodium polyphosphate, sodium  
30 hexametaphosphate, cesium hexametaphosphate, cesium polyphosphate ethoxy-(ethoxy-ethyl-phosphinothioylsulfanyl)-acetic acid ethyl ester, 1-fluoro-1-(2-hydroxy-phenoxy)-3-methyl-2,5-dihydro-1H-1λ5-phosphol-1-ol and water soluble functionalised silicon oil. Examples of inorganic salts include: mercury monosulphide, mercury(I) bromide, marcasite, calcite, sodium chlorate, lead  
35 monoxide, pyrite, lead(II) sulfide, copper(II) oxide, lithium fluoride, tin(IV) sulphide,

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lithium niobate and lead(II) nitrate. As insoluble compounds in water as well as in fluorinated and siloxane based fluids both inorganic, organic, and metallic nano particles may be used. The average size of the particles is preferably 10 times, more preferable 20 times, and even more preferably 30 times, and even more  
5 preferably 40 times smaller than the corresponding exposure wavelength. The average size of the nano particles may be less than 100 nanometer (nm), preferably less than 50 nm, more preferably less than 30 nm, still more preferably less than 20 nm, most preferably less than 10 nm. This results in a high transparency of the immersion fluid, especially at the wave length of the exposure  
10 light. The average size of the nano particles can be measured by Dynamic Light Scattering (DLS).

The volume percentage of the nano particles in the fluid is preferable at least 10%, more preferably at least 20%, still even more preferably at least 30%, even still more preferably at least 40%. Most preferably the volume  
15 percentage is at least 50%, as this results in a fluid having a high refractive index, a high transparency and low amount of scattering of the incident light. Examples of inorganic and metallic nano particles include: Alumina, , Aluminium nitride, Aluminium oxide, Antimony pent oxide, Antimony tin oxide, Brass, Calcium carbonate, Calcium chloride, Calcium oxide, Carbon black, Cerium, Cerium oxide,  
20 Cobalt, Cobalt oxide, Copper oxide, Gold, Hastelloy, Hematite- (alpha, beta, amorphous, epsilon, and gamma), , Indium tin oxide, , Iron-cobalt alloy, Iron-nickel alloy, Iron oxide, Iron oxide, transparent, Iron sulphide, Lanthanum, Lead sulphide, Lithium manganese oxide, Lithium titanate, Lithium vanadium oxide, Luminescent, Magnesite, Magnesium, Magnesium oxide, Magnetite, Manganese  
25 oxide, Molybdenum, Molybdenum oxide, Montmorillonite clay, Nano oxide suspensions, Nickel, Niobia, Niobium, Niobium oxide, Silicon carbide, Silicon dioxide preferably amorphous silicon dioxide, Silicon nitride, Silicon nitride, Yttrium oxide, Silicon nitride, Yttrium oxide, Aluminum oxide, Silver, Specialty, Stainless steel, Talc, Tantalum, Tin, Tin oxide, Titania, Titanium, Titanium  
30 diboride, Titanium dioxide, Tungsten, Tungsten carbide- cobalt, Tungsten oxide, Vanadium oxide, Yttria, Yttrium, Yttrium oxide, Zinc, Zinc oxide, Zirconium, Zirconium oxide and Zirconium silicate.

In a preferred embodiment nano particles comprising  $Al^{3+}$ - compounds are used in the immersion fluid of the process according to the  
35 invention. This is because such an immersion fluid has not only a very high

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refractive index, but is also highly transparent. Good examples of such particles include  $\text{Al}_2\text{O}_3$  preferably crystalline  $\alpha\text{-Al}_2\text{O}_3$  (Sapphire) and  $\text{Al}(\text{OH})_3$ .

This case good results are obtained if the immersion fluid comprises 25 - 65 vol.% of the nano particles comprising the  $\text{Al}^{3+}$ -compound. Preferably 25 - 45 vol%,  
5 more preferably 30 - 40 vol.% of the particles is used. Also good results are obtained by using nano particles of fused amorphous  $\text{SiO}_2$ , or nano particles comprising a mixture of fused amorphous  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$

Such immersion fluids not only has favorable optical properties, like a high refractive index and a high transparency, but is also well processable  
10 in the standard apparatus for producing microchips. For example the viscosity is low enough, so that the immersion fluid can be pumped easily.

It is known to the skilled person how to make stable dispersions of the nano particles in fluids like water.

It is also possible to use an immersion fluid in the process  
15 according to the invention, comprising a mixture of one or more soluble and one or more insoluble additives.

In a further preferred embodiment a fluid is used comprising transparent particles having a refractive index higher than the refractive index of the pure fluid and the additive in an amount, such that the refractive index of the  
20 fluid comprising the additive is equal to the refractive index of the transparent particles.

The transparent particles for example have an average diameter of 0.5 - 1000 microns. Preferably the transparent particles have an average diameter of 1 - 100 microns. Preferably 90 wt% of the transparent particles have a  
25 diameter between 0.1 and 10 microns, preferably between 4 and 10 microns.

Preferably the particles have a broad weight distribution and a spherical shape. In this way a high loading of the fluid with the transparent particles is possible, while the fluid still can be handled very well in the process for producing the chips, the fluid further having a very high transparency.

30 The weight percentage of particles in water containing the additive is preferably higher than 20%, more preferably higher than 40%, and even more preferably higher than 60%.

The transparency of the material of the transparent particles may be at least 40% (as measured over a theoretical light path of 1mm).

35 Preferably this transparency is at least 60%, more preferably at least 80%, still

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more preferably at least 90 %, most preferably at least 95%. Examples of suitable transparent particles are particles of transparent crystals, for example  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$ . Preferably amorphous  $\text{SiO}_2$  or sapphire particles are used.

More preferably particles of fused amorphous  $\text{SiO}_2$  are used,  
5 having a purity of at least 99 wt.%, more preferably at least 99.5 wt.%, still more preferably at least 99.9 wt.%. In this way a fluid having still further improved transparency is obtained

Examples of particles of fused amorphous  $\text{SiO}_2$  suitable for use in the immersion fluid are of the Lithosil™ series preferably Lithosil™Q0/1-E193  
10 and Lithosil™Q0/1-E248 (produced by Schott Lithotec), and fused amorphous  $\text{SiO}_2$  of the HPFS series with the Corning code 7980 (produced by Corning) as used for the production of lenses for apparatus for the production of chips. Such fused amorphous  $\text{SiO}_2$  is very pure and therefore may have a transparency of more than 99%. A method of producing such particles is by flame hydrolysis, a  
15 method known to the person skilled in the art.

In order to increase the refractive index of the particles of fused amorphous  $\text{SiO}_2$  it is possible to dope the particles with small amounts of suitable doping elements, for example Germanium.

In the fluid comprising the transparent particles, as the additive  
20 one or more of the above-referred soluble or insoluble additives may be used. Preferably an additive that is soluble in the fluid is used, preferably cesium sulphate, cesium hexametaphosphate or sodium hexametaphosphate..

In a further preferred embodiment a fluid is used comprising transparent particles which are functionalised on their surface in such a manner  
25 that they become dispersible in the immersion fluid. This is for example possible by grafting the particles with a surfactant, preferably a polymeric surfactant. It is also possible for purpose of dispersing the transparent particles to add a surfactant to the immersion fluid comprising the transparent particles.

In a preferred embodiment the method according to the  
30 invention comprises the steps of:  
a) measuring the refractive index of the immersion fluid directly or indirectly,  
b) adjusting the refractive index of the immersion fluid at a predetermined value by adding extra, pure fluid or adding extra additive to the immersion fluid.

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In this way fluctuations in the refractive index due to variations in temperature and concentration of the additive that increases the refractive index are compensated for.

The refractive index may be measured as such. It is also possible to measure one or more other parameters, being a measure for the refractive index. In case the immersion fluid comprises the transparent particles it is possible to determine the light scattering of the transparent particles and to add pure fluid or additive to reduce the light scattering. The addition of extra pure fluid may suitably be carried out by mixing extra pure fluid with the immersion fluid.

10 The addition of extra additive may suitably be carried out by mixing a concentrated solution of the additive in the pure fluid with the immersion fluid.

A still further preferred embodiment of the method according to the invention comprises the steps of

a) transporting the immersion fluid after being used in the production of a microchip to a cleaning unit,

15 b) cleaning the immersion fluid

c) recycling the cleaned immersion fluid into the process for producing the chips.

Due to the extraction of components from the photoresist layer on top of the wafer, possible chemical changes in the fluid components during the exposure step and further reasons, the immersion fluid will tend to be contaminated. This means that after a certain period of using the fluid in the process of the present invention, the fluid has to be refreshed. However this increases fluid consumption and negatively influences the process economics. Surprisingly it is possible to clean the fluid and recycle the cleaned fluid into the process of the present invention.

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Cleaning of the fluid is suitably carried out by cross flow filtration, or dead end flow filtration using for example membranes for micro or ultrafiltration or nanofiltration or reverse osmoses. Good results are obtained if a stirred pressure cell is used. An example of a stirred pressure cell is given in Fig. 1.

30

In Fig. 1 a stirred pressure cell is shown comprising a cell housing 1, having a stirrer 2, and an inlet for the used immersion fluid. Between the cell housing 1 and chamber 5 a membrane 3 is mounted. From gas cylinder 7, via pressured regulator 6 a pressure is applied on top of the fluid in cell housing 1. Due to this pressure fluid comprising contaminants is transported through the

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membrane in chamber 5 and transported further. In cell housing 1 a concentrated fluid composition comprising particles for example nano particles and/or transparent particles remains. Thereafter the refractive index of the concentrated fluid is adjusted to its original value again by adding pure fluid and if appropriate  
5 soluble additive.

The invention also relates to the immersion fluid. Preferably the immersion fluid has a transparency at one or more wavelength out of the group of 248, 193 and 157 nm of at least 10% through a path-length of 1mm, more preferably at least 20%, still more preferably at least 30%, even still more  
10 preferably at least 40%, most preferably at least 50%.

The invention also relates to an apparatus for immersion lithography for the production of microchips, comprising the immersion fluid.

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CLAIMS

1. Method for producing microchips by using immersion lithography,  
characterised in that the immersion fluid comprises an additive so that  
5 the refractive index of the immersion fluid is higher than the reflective  
index of the fluid not comprising the additive.
2. Method for producing microchips according to claim 1, characterised in  
that the refractive index is at least 1% higher.
3. Method according to claim 1 or 2, characterised in that the fluid  
10 comprises nano particles.
4. Method according to claim 3, characterized in that the particles have a  
diameter that is 10 times smaller than the wavelength of the exposure  
light.
5. Method according to any of claims 1-4, characterised in that the fluid  
15 comprises at least 10 volume % of nano particles.
6. Method according to any of claims 1-4, characterised in that the fluid  
comprises at least 50 volume % of nano particles.
7. Method according to any one of claims 1-6, characterized in that the fluid  
20 comprises transparent particles having a refractive index higher than the  
refractive index of the pure fluid and the additive in an amount, such that  
the refractive index of the fluid comprising the additive is equal to the  
refractive index of the transparent particles.
8. Immersion fluid as used in the method according to any one of claims 1-  
7.
- 25 9. Apparatus for producing microchips, based on the technology of  
immersion lithography, characterised in that the apparatus comprises the  
immersion fluid as used in the process of any one of claims 1-6.

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**ABSTRACT**

Method for producing microchips by using immersion lithography, wherein the immersion fluid comprises an additive so that the refractive index of the immersion fluid is increased relative to the fluid not comprising the additive. The exposure light in the method has improved resolution, so that microchips having an increased integration density are obtained. The invention also relates to the immersion fluid and an apparatus for immersion lithography, comprising the immersion fluid.

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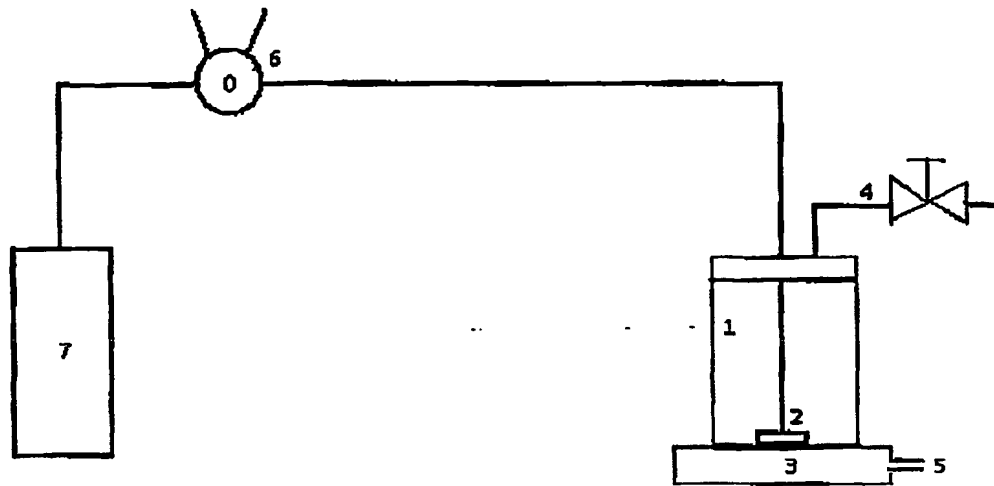


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